

(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 736 557 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
09.10.1996 Bulletin 1996/41

(51) Int. Cl.⁶: **C08G 63/16**, **C08L 67/02**,
C08L 3/02, **C08J 5/18**

(21) Application number: **96109981.9**

(22) Date of filing: **26.11.1991**

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(30) Priority: **30.11.1990 US 620225**
23.07.1991 US 736262
21.11.1991 US 797512

(62) Application number of the earlier application in
accordance with Art. 76 EPC: **92901494.2**

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Remarks:

This application was filed on 20 - 06 - 1996 as a
divisional application to the application mentioned
under INID code 62.

(54) **Aliphatic-aromatic copolyesters**

(57) This invention relates to random aliphatic-aromatic copolyesters, as well as fibers, molded objects, and films prepared therefrom.

EP 0 736 557 A1

Description

Field of Invention

This application is a divisional application of EP-A-0 559 785 (92 901 494.2).

This invention concerns random aliphatic-aromatic copolyesters which are useful as molded or extruded plastic objects, fibers, or films. Moreover, various additives can be added

to the random aliphatic-aromatic copolyesters to enhance properties such as water vapor transmission rates or biodegradability.

Background of the Invention

It is well known that cellulose esters are important as commercial plastics and as fibers. In general, cellulose esters are used in plastic applications where hard but clear plastics are required. For example, cellulose esters are used in tool handles, eyeglass frames, toys, toothbrush handles, and the like. All of these applications require a combination of high melting and glass transition temperatures as well as high modulus and good tensile strength. Formulations based on cellulose esters which provide plastic films with low modulus but good tensile strength while maintaining sufficient melting and glass transition temperatures (T_g) to allow thermal processing are generally unknown. Formulations based on cellulose esters which allow thermal extrusion of fibers are also generally unknown.

Because of the high melt temperatures and low melt stability of many of the cellulose esters, plasticizers such as dioctyl adipate or triphenylphosphate are often added to the cellulose ester to lower the melt temperatures during melt processing of the polymer. Although this technique is effective, addition of a monomeric plasticizer often creates secondary problems related to volatile or extractable plasticizers such as dye drip during melt extrusion or long-term dimensional stability (creep) in an object made from the cellulose ester.

The most basic requirement for polymer-polymer miscibility is that the free energy of mixing be negative ($\Delta G < 0$). Although on the surface it would seem that polymer-polymer miscibility would be common, in reality there are only a few known miscible binary blends and even fewer known miscible ternary blend systems (Brannock, G.R.; Paul, D.R., *Macromolecules*, 23, 5240-5250 (1990)). The discovery of miscible binary or ternary blends is very uncommon.

The classical experimental techniques for determining polymer blend miscibility involve the determination of the optical clarity of a film made from the blend, measurement of the appropriate mechanical properties, and measurement of the glass transition temperature by an appropriate thermal analysis technique such as dynamic mechanical thermal analysis (DMTA) or differential scanning calorimetry (DSC). If a blend is miscible, films made from the blend will generally be clear. Likewise, mechanical properties of a blend, such as tensile strength or tangent modulus, are often intermediate between those of the blend components. Furthermore, a miscible amorphous blend will show a single T_g intermediate between that of the component homopolymers while an immiscible or partially miscible blend will show multiple T_g's. In the case of a completely immiscible blend, the T_g's will be those of the homopolymers. For partially miscible blends, the T_g's will be intermediate values corresponding to partially miscible phases rich in one of the components. The variation in binary blend T_g can be modeled by the Fox-Flory equation, $T_{g12} = T_{g1}(W_1) + T_{g2}(W_2)$, where T_{g12} is the T_g of the blend, T_{g1} and T_{g2} are the T_g's of homopolymers, and W₁ and W₂ are the weight percent of each component in the blend. Since the Fox equation does not take into account specific interaction between the blend components the Gordon-Taylor equation, $T_{g12} = T_{g1} + [kW_2(T_{g2} - T_{g12})/W_1]$ where k is a constant, is often preferred in blend analysis. For a homogenous, well mixed system, a plot of T_{g12} versus $W_2(T_{g2} - T_{g12})/W_1$ will yield a straight line the slope of which is equal to k and the ordinate intercept will be equal to T_{g1}. The constant k is often taken as a measure of secondary interactions between the blend components. When k is equal to one, the Gordon-Taylor equation reduces to a simple weight average of the component T_g's.

Miscible blends of cellulose esters and other polymers are generally unknown. The most notable exceptions include the work disclosed by Koleske, et al. (U.S. Patent 3,781,381 (1973)), Bogan and Combs (U.S. Patent 3,668,157 (1972)), Waniczek et al., (U.S. Patent 4,506,045 (1985)), and Wingler et al. (U.S. Patent 4,533,397 (1985)). Koleske et al. reported that blends, formed by solution casting of polycaprolactone and cellulose ester mixtures, are miscible. Later work by Hubbell and Cooper (*J. Appl. Polym. Sci.*, 1977, 21, 3035) demonstrated that cellulose acetate butyrate/polycaprolactone blends are in fact immiscible. Bogan and Combs have reported that block copolymers of polyether/polyesters form miscible blends with some cellulose esters. Critical to the invention of Bogan and Combs was the use of an elastomeric block copolymer; they report that the corresponding homopolymeric elastomers were incompatible with cellulose esters. Waniczek et al., have disclosed that polyester carbonates and polyether carbonates copolymers form miscible blends with many cellulose esters and are useful as thermoplastic resins. Wingler et al. report that contact lenses can be prepared from blends consisting of (A) 97-70% by weight of one or more cellulose esters and (B) 3-30% by weight of an aliphatic polymeric compound having ester moieties, carbonate moieties, or both ester and carbonate moieties in the same polymer chain. The invention of Wingler et al. is limited to aliphatic polymeric compounds; no reference is made to random copolymers consisting of aliphatic diacids, aromatic diacids, and suitable diols or polyols.

The invention of Wingler is further limited to cellulose mixed esters having a weight per cent hydroxyl of 1.2% to 1.95% ($DS_{OH} = 0.11-0.19$ where "DS" or "DS/AGU" refers to the number of substituents per anhydroglucose unit where the maximum DS/AGU is three). The invention of Wingler et al. is also limited to binary miscible blends and by the composition range of the blends (3-30% aliphatic polymeric compound). No reference is made to blends containing an immiscible component where the immiscible component is useful for enhancing properties such as water vapor transmission rates or biodegradability. Immiscible blends of cellulose esters and aromatic polyesters have also been disclosed by Pollock et al. (U.S. Patent 4,770,931 (1988)) which are useful in applications such as paper substitutes.

One time use, disposable items are common. Examples of such disposable articles include items such as infant diapers, incontinence briefs, sanitary napkins, tampons, bed liners, bedpans, bandages, food bags, agricultural compost sheets, and the like. Examples of other disposable items include razor blade handles, toothbrush handles, disposable syringes, fishing lines, fishing nets, packaging, cups, clamshells, and the like. For disposable items, environmental non-persistence is desirable.

Disposable articles are typified by disposable diapers. A disposable diaper typically has a thin, flexible polyethylene film cover, an absorbent filler as the middle layer, and a porous inner liner which is typically nonwoven polypropylene. The diaper construction also requires tabs or tape for fastening the diaper (typically polypropylene) as well as various elastomers and adhesives. Although the absorbent filler is usually biodegradable or easily dispersed in an aqueous environment, currently neither the outer or inner liner nor the other parts such as the tabs or adhesives will degrade from microbial action. Consequently, disposable absorbent materials such as diapers accumulate in landfills and place enormous pressure on waste systems. Other disposable articles such as plastic bags or plastic compost sheets suffer from similar problems.

Numerous studies have demonstrated that cellulose or cellulose derivatives with a low degree of substitution, i.e., less than one, are biodegradable. Cellulose is degraded in the environment by both anaerobic or aerobic microorganisms. Typical endproducts of this microbial degradation include cell biomass, methane (anaerobic only), carbon dioxide, water, and other fermentation products. The ultimate endproducts will depend upon the type of environment as well as the type of microbial population that is present. However, it has been reported that cellulose esters with a DS greater than about one are completely resistant to attack by microorganisms. For example, Stutzenberger and Kahler (*J. Appl. Bacteriology*, 66, 225 (1986)) have reported that cellulose acetate is extremely recalcitrant to attack by *Thermomonospora curvata*.

Polyhydroxyalkanoates (PHA), such as polyhydroxybutyrate (PHB), polycaprolactone (PCL), or copolymers of polyhydroxybutyrate and polyhydroxyvalerate (PHBV), have been known for at least twenty years. With the exception of polycaprolactone, they are generally prepared biologically and have been reported to be biodegradable (M. Kunioka et al., *Appl. Microbiol. Biotechnol.*, 30, 569 (1989)).

Polyesters prepared from aliphatic diacids or the corresponding carboxylic ester of lower alcohols and diols have also been reported to be biodegradable. For example, Fields and Rodriguez ("Proceedings of the Third International Biodegradation Symposium", J.M. Sharpley and A.M. Kaplan, Eds., Applied Science, Barking, England, 1976, p. 775) prepared polyesters from C2-C12 diacids coupled with C4-C12 diols and found that many were biodegradable.

Aliphatic polyesters have been used in very few applications mainly because of their low melting points and low glass transition temperatures (generally less than 65°C and -30°C, respectively). At room temperature, the physical form of many of the aliphatic polyesters is as a thick, viscous liquid. Therefore, aliphatic polyesters are not expected to be generally useful.

On the other hand, aromatic polyesters, such as poly(ethylene terephthalate), poly(cyclohexanedimethanol terephthalate), and poly(ethylene terephthalate-co-isophthalate), have proven to be very useful materials. Aromatic polyesters, however, are generally very resistant to biodegradation (J. E. Potts in "Kirk-Othmer Encyclopedia of Chemical Technology", Suppl. Vol, Wiley-Interscience, New York, 1984, pp. 626-668). Block copolymers containing both aliphatic and aromatic structures have been prepared and have been shown to be biodegradable. Examples of aliphatic-aromatic block copolyester-ethers include the work of Reed and Gilding (*Polymer*, 22, 499 (1981)) using poly(ethylene terephthalate)/poly(ethylene oxide) where these block copolymers were studied and found to be biodegradable in vitro. Tokiwa and Suzuki have investigated block copolymers such as those derived from poly(caprolactone) and poly(butylene terephthalate) and found them to be degraded by a lipase (*J. Appl. Polym. Sci.*, 26, 441-448 (1981)). Presumably, the biodegradation is dependent upon the aliphatic blocks of the copolymers; the blocks consisting of aromatic polyester are still resistant to biodegradation. Random aliphatic-aromatic copolymers have not been investigated in this regard.

While random copolymers with low levels of aliphatic diacids are known (e.g., Droscher and Horlbeck, *Angew. Makromol. Chemie*, 128, 203-213(1984)), copolymers with high levels (>30%) of aliphatic dicarboxylic components are generally unknown. Copolymers with as much as 40% aliphatic dicarboxylic acid components have been disclosed in adhesive applications; however, these copolymers adhesives contain at least two dialcohol components in order to achieve the desired adhesive properties (Cox, A., Meyer, M. F., U.S. Patent No. 4,966,959 (1990)).

There are many references to the preparation of films from polymers such as polyhydroxybutyrate (PHB). Production of films from PHB generally involves solvent casting principally because PHB polymers tend to remain sticky or

tacky for a substantial time after the temperature has dropped below the melting point of the PHB. To circumvent this problem, Martini et al. (U.S. Patents 4,826,493 and 4,880,592) teach the practice of co-extruding PHB with a thermoplastic that is non-tacky. Such thermoplastics remain as a permanent layer on the PHB film or may be a sacrificial film which is removed following extrusion.

PHB has also been reported to be useful in the preparation of disposable articles. Potts (U.S. Patents 4,372,311 and 4,503,098) has disclosed that water soluble polymers such as poly(ethylene oxide) may be coated with biodegradable water insoluble polymers such as PHB. In these inventions, the PHB layer, which is distinct from the water soluble layer, degrades exposing the water soluble layer which will then disperse in an aqueous environment.

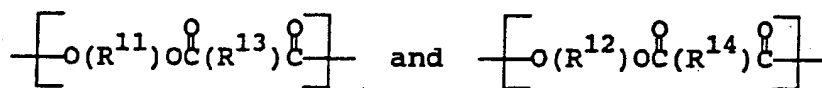
There have been other reports of the preparation of a biodegradable barrier film for use in disposable articles. Comerford et al. (U.S. Patent 3,952,347) have disclosed that finely divided biodegradable materials such as cellulose, starch, carbohydrates, and natural gums may be dispersed in a matrix of nonbiodegradable film forming materials which are resistant to solubility in water. Wielicki (U.S. Patent 3,602,225) teaches the use of barrier films made of plasticized regenerated cellulose films. Comerford (U.S. Patent 3,683,917) teaches the use of a cellulosic material coated with a water repellent material.

There exists in the market place the need for thermoplastics which are useful in molding, fiber, and film applications. For these applications, it is desirable that the thermoplastic blend be processable at a low melt temperature and have a high glass transition temperature. These thermoplastics should not contain volatile or extractable plasticizers. Moreover, there is a need in the marketplace for a biodegradable material for use in disposable articles such as diapers, razors, and the like. As an example, unlike films prepared from polymers such as PHB, the material should be amenable to both solvent casting and melt extrusion. In melt extruding this material, coextrusion with other thermoplastics should not be a requirement. The barrier properties of this new biodegradable material should be adequate so that coating with a water insoluble polymer is not required. The new material should disperse completely in the environment and not require coating with a water soluble polymer. The mechanical properties of the material should be such that films of low modulus but of high tensile strength can be prepared.

Summary of the Invention

The present invention concerns random aliphatic-aromatic copolyesters as defined in more detail below and in the claims.

The aliphatic-aromatic copolyesters (referred to as AAPE herein) that are useful in the present invention without requiring blending of a significant amount of another component are essentially linear, random copolymers and comprise repeating units of:



wherein R^{11} and R^{12} are the same and are selected from the groups consisting of C2-C8 alkylene or oxyalkylene; R^{13} is selected from one or more of the groups consisting of C0-C8 alkylene or C2-C4 oxyalkylene, and the mole % of R^{13} is from about 95-35%; R^{14} is selected from the group of C6-C10 aryl, and the mole % of R^{14} is from about 5-65%. More preferred AAPE are those wherein R^{11} and R^{12} are the same and are selected from C2-C4 alkylene R^{13} is selected from one or more of the groups consisting of C2-C6 alkylene or C2 oxyalkylene, and the mole % of R^{13} is from about 95-40%; R^{14} is 1,4-disubstituted-C6 aryl, and the mole % of R^{14} is from about 5-60%. The most preferred compositions for these AAPE are those prepared from the following diols and diacids (or polyester forming derivatives thereof) in the following mole %:

- (1) Glutaric acid (30-65%); diglycolic acid (0-10 mol%); terephthalic acid (25-60%); 1,4-butanediol (100 mole%).
- (2) Succinic acid (30-85%); diglycolic acid (0-10%); terephthalic acid (5-60%); 1,4-butanediol (100 mole%).
- (3) Adipic acid (30-65%); diglycolic acid (0-10%); terephthalic acid (25-60%); 1,4-butanediol (100 mole%).

Specific examples of preferred AAPE for applications where blending is not required include poly(tetramethylene glutarate-co-terephthalate-co-diglycolate) [50/45/5], poly(tetramethylene glutarate-co-terephthalate) [50/50], poly(tetramethylene glutarate-co-terephthalate) [60/40], poly(tetramethylene glutarate-co-terephthalate) [40/60], poly(tetramethylene succinate-co-terephthalate) [85/15], poly(ethylene succinate-co-terephthalate) [70/30], poly(tetramethylene adipate-co-terephthalate) [85/15], and poly(tetramethylene succinate-co-terephthalate) [70/30].

Of course, many of the AAPEs of this invention which do not require blending are also useful in film applications. While these AAPE do not have as high a melting point as poly(ethylene terephthalate), the AAPE have higher melt-

ing points that are generally observed with aliphatic polyesters and are therefore useful in many applications, particularly those requiring biodegradability. Succinic acid based AAPEs show particularly good utility in these applications due to their relatively high melting points. These copolyesters have been shown to be degradable even though they are semicrystalline and contain substantial amounts of aromatic groups. Furthermore, diglycolic acid has been found to be a useful comonomer for these AAPE because it aids in the initial breakup of the films.

These AAPEs are also particularly useful in molded parts, extruded objects, fibers, non-wovens, and foamed objects which benefit from being biodegradable. Films and fibers made from these copolyesters can be oriented. Orientation in many of these copolymers (especially those containing 1,4-butanediol) is accompanied by improved physical properties and a change from being opaque to being clear. AAPE films can be oriented uniaxially or biaxially and can be oriented in a blown film operation.

The AAPEs of this invention are useful in packaging applications where thin films are desirable. Many of the AAPEs of this invention are particularly useful as thin barrier films where they must function as a barrier and/or be biodegradable. For example, these AAPEs are useful as protective barrier films and may be used in disposable absorbent articles such as infant diapers, incontinence briefs, sanitary napkins, tampons, bed liners, bedpan liners, bandages, and the like. It is preferred that the films of the invention have a tangert modulus of 2.5×10^5 psi to 0.01×10^5 psi, a tensile strength of at least about 0.5×10^3 psi, an average tear force of at least about 7.0 g/mil, and an elongation at break of at least about 5%. Also preferred is wherein said films have a thickness of 0.1 mil to 20 mil and a water vapor transmission rate less than about 500 g mil/m²-24 hours.

The AAPEs of this invention can also be used in the other parts of disposable diapers. In addition to being used as a protective barrier film, these blends and/or AAPEs can be used as tabs, nonwovens, fibers, tape, and other parts needed in the construction of a diaper.

We have found that films prepared from these AAPEs have desirable moisture barrier properties. With the blends, the specific rates can be modified by modification of the blend composition.

The water vapor transmission rates can also be controlled by the amount of aromatic dicarboxylic acid monomer present in the aliphatic-aromatic copolyester component.

The AAPEs of this invention are also useful as molded plastic parts or as solid, foamed plastic objects. Examples of such parts include eyeglass frames, toothbrush handles, toys, automotive trim, tool handles, camera parts, razor parts, ink pen barrels, disposable syringes, bottles, and the like. The plastic parts, especially those made by a foamed method which gives the plastic part increased surface area, of this invention are particularly useful in applications where it is desired that the plastic part be environmentally non-persistent. Injection molding bars made from the of the invention typically have a flexural modulus of 5.0×10^5 psi to 0.1×10^5 psi, a flexural strength of 13×10^3 psi to 0.1×10^3 psi, and a notched Izod (23°C) of 1.0 to 25 ft-lb/in. It is preferred that the molding bars have a flexural modulus of 3.8×10^5 psi to 1.5×10^5 psi, a flexural strength of 11.4×10^3 psi to 4×10^3 psi, and a notched Izod (23°C) of 2 to 15 ft-lb/in.

The of this invention are also useful as fibers. Examples of fiber applications include cigarette filters, diaper top-sheet, sanitary napkins, fishing line, fishing nets, fiber for producing surgical clothing, hygiene articles, absorbent fibers, fibers for conveying liquids, and the like. We have found that, in addition to being spun from an appropriate solvent, the blends and/or AAPE of this invention can be melt-spun to produce fibers with excellent strength. The fibers can be oriented by drawing the fiber after spinning or by orientation during the spinning (cabinet orientation). Fibers produced from the blends and/or AAPEs have excellent shape retention even for fibers with complex cross-sectional shapes. We have also found that the fibers can be readily crimped. Fiber produced from the blends and/or AAPEs typically have a denier/filament (DPF) of 30-0.1. The preferred denier is 10-1.5 DPF. For fluid management, the fiber can contain hydrophobic agents or, optionally, can be coated with hydrophobic agents.

The blends, films, plastic objects, and fibers prepared from the blends of the invention have a melt temperature between 120°C and 280°C. The preferred melt temperature range from 150°C to 190°C. Also, such blends, films, plastic objects, and fibers have a glass transition temperature (T_g) as measured by differential scanning calorimetry (DSC) or dynamic mechanical thermal analysis (DMTA) of about 25°C to about 200°C. The preferred range for the glass transition temperatures is 50°C to 100°C. The blends and films are also preferably non-tacky.

The preferred AAPE of this invention and products made therefrom have melting points between 75°C and 160°C. The more preferred range is between 80°C and 140°C.

The fibers and films prepared from the of the present invention are useful in applications where protective barrier films are desirable. For example, they may be used in absorbent articles such as infant diapers, incontinence briefs (adult diapers), sanitary napkins, tampons, bed liners, bedpans, bandages, and the like. The biodegradable films, fibers, and AAPE of the invention are particularly useful in disposable articles because of environmental considerations. The films of the invention can also be used to make non-absorbent articles such as packaging materials (for example, foam sheets for packaging), food bags, trash bags, agricultural compost sheets, film base for tape and photographic film, as well as solid plastic articles such as syringes and camera cases.

Biodegradable materials, such as the preferred barrier films of this invention, are materials that are comprised of components which, by microbial catalyzed degradation, are reduced in film or fiber strength by reduction in polymer size to monomers or short chains which are then assimilated by the microbes. In an aerobic environment, these monomers

or short chains are ultimately oxidized to CO₂, H₂O, and new cell biomass. In an anaerobic environment the monomers or short chains are ultimately oxidized to CO₂, H₂, acetate, methane, and cell biomass. Successful biodegradation requires that direct physical contact must be established between the biodegradable material and the active microbial population or the enzymes produced by the active microbial population. An active microbial population useful for degrading the films and blends of the invention can generally be obtained from any municipal or industrial wastewater treatment facility in which the influents (waste stream) are high in cellulose materials. Moreover, successful biodegradation requires that certain minimal physical and chemical requirements be met such as suitable pH, temperature, oxygen concentration, proper nutrients, and moisture level. We have found that certain cellulose esters are biodegradable in conventional wastewater treatment facilities and in an *in vitro* enrichment system and hence are particularly useful in the preparation of blends to be used for barrier films and fibers in disposable articles. We have also found that many of the blends and AAPE degrade in a composting environment and hence are useful in the preparation of materials to be used as environmentally nonpersistent materials.

The following examples are to illustrate the invention but should not be interpreted as a limitation thereon.

The tensile strength, break to elongation, and tangent modulus of the films are measured by ASTM method D882; the tear force is measured by ASTM method D1938; the oxygen and water vapor transmission rates are measured by ASTM methods D3985 and F372, respectively. The tensile strength and elongation at break for molded pieces are measured by ASTM method D638; the flexural strength and modulus by ASTM method D790; the Izod impact strength by ASTM method D256; the heat deflection temperature by ASTM method D648. Inherent viscosities are measured at a temperature of 25°C for a 0.5 gram sample in 100 ml of a 60/40 by weight solution of phenol/tetrachloroethane. Dynamic mechanical thermal analysis (DMTA) spectra were collected using a Polymer Laboratories Mk II at 4°C/min and 1 Hz.

Abbreviations used herein are as follows: "IV" is inherent viscosity; "g" is gram; "psi" is pounds per square inch; "cc" is cubic centimeter; "m" is meter; "rpm" is revolutions per minute; "DSPr" is degree of substitution per anhydroglucose unit for propionyl; "DSAc" is degree of substitution per anhydroglucose unit for acetyl; "DSBu" is degree of substitution per anhydroglucose unit for butyryl; "BOD" is biochemical oxygen demand; "vol." or "v" is volume; "wt." is weight; "mm" is micrometer; "NaOAc" is sodium acetate; "nm" is not measured; "CE" is cellulose ester; "PE" is polyester; "DOA" is dioctyl adipate; "HDT" is heat deflection temperature; "WVTR" is water vapor transmission rate; "mil" is 0.001 inch. Relative to the clarity of the films, "+" indicates a transparent film characteristic of a miscible blend; "±" indicates a hazy film characteristic of a partially miscible film; "-" indicates an opaque film characteristic of an immiscible blend; "AAPE" is aliphatic-aromatic copolyester and, as used herein, refers to the copolyesters where blending is not required. Relative to naming of the cellulose ester, "CAP" is cellulose acetate propionate; "CA" is cellulose acetate; "CAB" is cellulose acetate butyrate. Relative to naming of the polyester, representative examples are: "PTS(T) [85/15]" is poly(tetramethylene succinate-co-terephthalate) where the mole per cent of succinate to terephthalate is 85/15; "PTA(T) [85/15]" is poly(tetramethylene adipate-co-terephthalate) where the mole per cent of adipate to terephthalate is 85/15; "PTG(T) [85/15]" is poly(tetramethylene glutarate-co-terephthalate) where the mole per cent of glutarate to terephthalate is 85/15; "PTG(T)(D) [60/35/5]" is poly(tetramethylene glutarate-co-terephthalate-co-diglycolate) where the mole per cent of glutarate to terephthalate to diglycolate is 60/35/5; "PTG(N) [85/15]" is poly(tetramethylene glutarate-co-naphthalate) where the mole per cent of glutarate to naphthalate is 85/15; "PES" is poly(ethylene succinate); "PHS" is poly(hexamethylene succinate); "PEG" is poly(ethylene glutarate); "PTG" is poly(tetramethylene glutarate); "PHG" is poly(hexamethylene glutarate); "PT(E)G [50/50]" is poly(tetramethylene-co-ethylene glutarate) where the mole % of tetramethylene to ethylene is 50/50; "PEA" is poly(ethylene adipate); "PDEA" is poly(diethylene adipate); "PHA" is poly(hexamethylene adipate). Other abbreviations are: "TEGDA" is triethylene glycol diacetate; "PVA" is poly(vinyl acetate); "PMMA" is poly(methyl methacrylate); "PEMA" is poly(ethyl methacrylate). MYVAPLEX 600 is the trade name for concentrated glyceryl monostearates and is available from Eastman Chemical Company. MYVAPLEX concentrated glyceryl monostearate is a 90% minimum distilled monoglyceride produced from hydrogenated soybean oil which is composed primarily of stearic acid esters. MYVACET is the trade name for distilled acetylated monoglycerides of modified fats. The per cent acetylation of MYVACET 507 ranges from 48.5 to 51.5; the per cent acetylation of MYVACET 707 ranges from 66.5 to 69.5; the per cent acetylation of MYVACET 908 is a minimum of 96. MYVEROL is the trade name for concentrated glyceryl monostearates and is available from Eastman Chemical Company. MYVEROL is very similar to MYVAPLEX except that the distilled monoglyceride is produced from different fat sources.

EXAMPLE 1

Table I

Inherent Viscosity, Water Vapor Transmission Rates, Mechanical Properties, and Tear Strength of Films Prepared From Aliphatic-Aromatic Copolyesters							
Entry	Polyester	Elongation at Break (%)	Tangent Modulus (10^5 psi)	Tensile Strength (10^3 psi)	Tear Strength (g/mil)	IV	WVTR (g/100 in ² -24 hours)
160	PHG(T) [50/50]	357	0.09	0.73	26	0.72	65
161	PTG(T) [60/40]	908	0.05	1.95	214	1.15	137
162	PTG(T) [40/60]	642	0.23	3.07	115	0.94	52
163	PTS(T) [70/30]	722	0.41	4.48	59	nm	nm
164	PTS(T) [85/15]	732	0.28	3.99	42	1.03	42
165	PTG(T) [55/45]	738	0.08	3.54	142	1.11	nm
166	PTG(T)(D) [50/45/5]	927	0.05	5.22	126	1.23	nm

These examples illustrate that films prepared from aliphatic-aromatic copolyesters have very high elongation, high tear strengths, low WVTR, and low moduli and hence are useful in film applications.

EXAMPLE 2 - The physical properties of AAPE molded bars

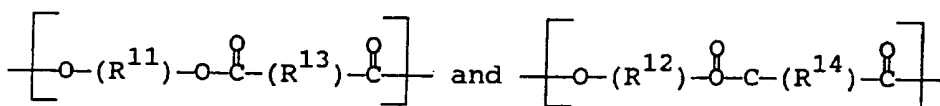
Table II

Physical Properties of AAPE			
Property (units)	PTS(T) [85/15]	PTS(T) [70/30]	PTG(T) [50/50]
Tensile Strength (10^3 psi)	2.89	1.79	1.51
Elongation at break (%)	482	384	437
Flexural Modulus (10^5 psi)	0.57	0.20	0.13
Izod Impact 23°C (ft-lb/in)	6.0 (NB)	6.5 (NB)	3.2 (NB)
Izod Impact -40°C (ft-lb/in)	0.44 (CB)	0.86 (CB)	8.23 (NB)

This example demonstrates that AAPEs have very high elongation at break, low flexural modulus and excellent Izod Impacts.

Claims

1. An essentially linear, random, semicrystalline aliphatic-aromatic copolyester which has an inherent viscosity of at least 0.4 deciliters/gram as measured at a temperature of 25°C for a 0.5 g sample in 100 mL of a 60/40 parts by weight solution of phenol/tetrachloroethane wherein the aliphatic-aromatic copolyester is comprised of repeat units of the following structures:



wherein R^{11} and R^{12} are the same and are selected from the groups C2-C8 alkylene or oxyalkylene wherein R^{11} and R^{12} are 100% of the diol components; R^{13} is selected from one or more of the groups consisting of C0-C8 alkylene or C2-C4 oxyalkylene wherein the mole % of R^{13} is from 35-95% of the dicarboxylic components; and R^{14} is selected from the group consisting of C6-C10 aryl wherein the mole % of R^{14} is from 5-65% of the dicarboxylic component.

2. The aliphatic-aromatic copolyester of Claim 1 wherein R^{11} and R^{12} are the same and are selected from the groups C2-C6 alkylene wherein R^{11} and R^{12} are 100% of the diol components; R^{13} is selected from one or more of the groups consisting of C2-C4 alkylene or C2 oxyalkylene wherein the mole % of R^{13} is from 40-95% of the dicarboxylic components; R^{14} is a 1,4-disubstituted C6 aryl wherein the mole % of R^{14} is from 5-60% of the dicarboxylic components.
3. The aliphatic-aromatic copolyester of Claim 1 wherein R^{11} and R^{12} are the same and are selected from the groups consisting of C4 and C6 alkylene wherein R^{11} and R^{12} are 100% of the diol components; R^{13} is selected from one or more of the groups consisting of C3-C4 alkylene wherein the mole % of R^{13} is from 40-60% of the dicarboxylic components; R^{14} is selected from the group consisting of C6-C10 aryl wherein the mole % of R^{14} is from 60-40% of the dicarboxylic components.
4. The aliphatic-aromatic copolyester of Claim 1 which has a melting point of 75°C to 160°C.
5. The aliphatic-aromatic copolyester of Claim 4 where C4 is selected for R^{11} and R^{12} at an amount of 100 mol%; where C3 and $-\text{CH}_2-\text{O}-\text{CH}_2-$ are selected for R^{13} at an amount of 30 to 65 mole% and 0 to 10 mole %, respectively; and where a 1,4-disubstituted aryl is selected for R^{14} at an amount of 25 to 60%.
6. The aliphatic-aromatic copolyester of Claim 4 where C4 is selected for R^{11} and R^{12} at an amount of 100 mol%; where C2 and $-\text{CH}_2-\text{O}-\text{CH}_2-$ are selected for R^{13} at an amount of 30 to 85 mole% and 0 to 10 mole%, respectively; where a 1,4-disubstituted aryl is selected for R^{14} at an amount of 5 to 60%.
7. The aliphatic-aromatic copolyester of Claim 4 where C4 is selected for R^{11} and R^{12} at an amount of 100 mol%; where C4 and $-\text{CH}_2-\text{O}-\text{CH}_2-$ are selected for R^{13} at an amount of 30 to 65 mole% and 0 to 10 mole%, respectively; and where a 1,4-disubstituted aryl is selected for R^{14} at an amount of 25 to 60%.
8. The aliphatic-aromatic copolyester of Claim 4 wherein the aliphatic-aromatic copolyester is poly(tetramethylene glutarate-co-terephthalate) copolyester wherein the mole % of terephthalate is 45-60%.
9. The aliphatic-aromatic copolyester of Claim 4 wherein the aliphatic-aromatic copolyester is poly(tetramethylene succinate-co-terephthalate) copolyester wherein the mole % of terephthalate is 5-30%.
10. The aliphatic-aromatic copolyester of Claim 4 wherein the aliphatic-aromatic copolyester is poly(ethylene succinate-co-terephthalate) copolyester wherein the mole % of terephthalate is 5-20%.
11. The aliphatic-aromatic copolyester of Claim 4 wherein the aliphatic-aromatic copolyester is poly(ethylene adipate-co-terephthalate) copolyester wherein the mole % of terephthalate is 40-60%.
12. The aliphatic-aromatic copolyester of Claim 4 wherein the aliphatic-aromatic copolyester is poly(tetramethylene adipate-co-terephthalate) copolyester wherein the mole % of terephthalate is 40-60%.
13. The aliphatic-aromatic copolyester of Claim 4 wherein the aliphatic-aromatic copolyester is poly(hexamethylene adipate-co-terephthalate) copolyester wherein the mole % of terephthalate is 40-60%.

14. The aliphatic-aromatic copolyester of Claim 4 wherein the aliphatic-aromatic copolyester is poly(tetramethylene glutarate-co-terephthalate-co-diglycolate) copolyester wherein the mole % of terephthalate is 45-60% and the mole % of diglycolate is 1-10 mole %.
- 5 15. The aliphatic-aromatic copolyester of Claim 4 wherein the aliphatic-aromatic copolyester is poly(tetramethylene succinate-co-terephthalate-co-diglycolate) copolyester wherein the mole % of terephthalate is 5-30% and the mole % of diglycolate is 1-10 mole %.
- 10 16. The aliphatic-aromatic copolyester of Claim 1 additionally comprising 0.001 to 50 weight %, based on the total weight of the composition, of at least one additional additive selected from a non-polymeric plasticizer, a thermal stabilizer, an antioxidant, a pro-oxidant, an acid scavenger, an ultraviolet light stabilizer, a promoter of photodegradation, inorganics, and colorants.
- 15 17. The aliphatic-aromatic copolyester of Claim 1 wherein the aliphatic-aromatic copolyester is used in the form of a shaped article.
18. The aliphatic-aromatic copolyester of Claim 17 wherein said shaped articles is selected from the group consisting of films, fibers or plastic objects.
- 20 19. The aliphatic-aromatic copolyester of Claim 18 wherein said shaped article is a plastic film.
20. The aliphatic-aromatic copolyester of Claim 19 in the form of a plastic film having a tangent modulus of 2.5×10^5 psi to 0.01×10^5 psi, a tensile strength of at least 0.5×10^3 psi, an average tear force of at least 7 g/mil, and an elongation at break of at least 5%.
- 25 21. The aliphatic-aromatic copolyester of Claim 19 in the form of a film having a thickness of 0.1 mil to 20 mil and a water vapor transmission rate less than 500 g mil/m²-24 hours.
22. The aliphatic-aromatic copolyester of Claim 19 wherein said film is prepared by solvent casting, melt extrusion, or by a blown film process.
- 30 23. The aliphatic-aromatic copolyester of Claim 22 wherein said film is oriented during a blow film process.
24. The aliphatic-aromatic copolyester of Claim 22 wherein said film is melt extruded and then uniaxially or biaxially oriented.
- 35 25. The aliphatic-aromatic copolyester of Claim 17 wherein the shaped articles are biodegradable.
26. The aliphatic-aromatic copolyester of Claim 1 wherein molded bars made from the blends have a flexural modulus of 5.0×10^5 psi to 0.1×10^5 psi, a flexural strength of 13×10^3 psi to 0.1×10^3 psi, and a notched Izod (23°C) of 1.0 to 25 ft-lb/in.
- 40 27. A blend comprising:
 - 45 (A) 50% to 99% of an aliphatic-aromatic copolyester according to any one of Claims 1 to 15 and having an inherent viscosity of at least 0.4 deciliters/gram as measured at a temperature of 25°C for a 0.5 g sample in 100 ml of a 60/40 parts by weight solution of phenol/tetrachloroethane,
 - (B) 1% to 50% of biodegradable additives, said percentages being based on the weight of component (A) plus component (B).
- 50 28. The blend of Claim 27, wherein component (B) is starch.
29. The random aliphatic-aromatic copolyester of Claim 1 comprising repeating units derived from either components (a) or (b) as follows:
 - 55 (a) a diol component comprising said R11 and R12 and an acid component comprising said R13 wherein said R13 represents an aliphatic polycarboxylic acid, and

EP 0 736 557 A1

(b) a diol comprising said R11 and R12 and an acid component comprising said R14 wherein said R14 represents an aromatic polycarboxylic acid and further wherein 20% - 99% of the repeating units of (a) are either not directly coupled with another repeating unit of (a) or are directly coupled with only one repeating unit of (a).

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EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 96109981.9
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X, Y	<u>US - A - 4 419 507</u> (SUBLETT) * Claims; table II; column 6, lines 41-46; column 10, lines 12-13 * --	1-4, 7, 11, 12, 16-19, 29	C 08 G 63/16 C 08 L 67/02 C 08 L 3/02 C 08 J 5/18
Y	<u>EP - A - 0 388 924</u> (E.R. SQUIBB & SONS, INC.) * Claims * --	1, 16-19, 22, 25, 27, 28	
X	<u>US - A - 4 328 059</u> (HORLBECK et al.) * Claim 1; column 2, lines 19-35; column 3, lines 39-41 * --	1-15, 29	
X	<u>GB - A - 1 515 727</u> (DYNAMIT NOBEL AG) * Claims 1, 24; page 10, lines 44-52; tables 1, 2 * --	1-4, 7, 11, 12, 16-19, 29	
X	<u>FR - A - 1 045 649</u> (E.I. DU PONT DE NEMOURS) * Claims; examples 1-3, 4, 6, 12-14 * --	1, 17- 19, 29	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 08 G 63/00 C 08 L 67/00 C 08 L 3/00 C 08 J B 32 B
X	<u>US - A - 4 436 895</u> (BARBEE et al.) * Claims 1-4, 6-11; table II, last entry * ----	1, 17	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 01-08-1996	Examiner WEIGERSTORFER
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 (03/93) (1/9601)